Supporting Information

Template-Free Nanostructured Fluorine-Doped Tin Oxide Scaffolds for Photoelectrochemical Water Splitting

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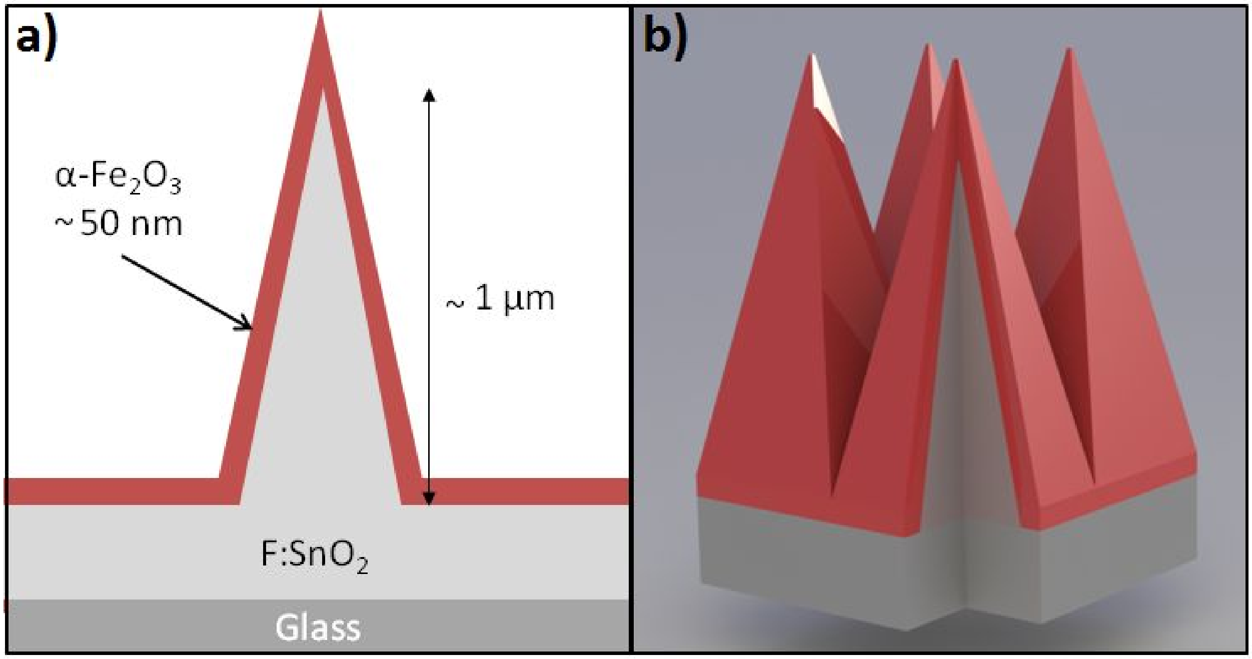

Figure S1. a) Schematic representation of a nano-pyramid fluorine-doped tin oxide (FTO) scaffold coated with an ultra-thin α-Fe_2O_3 film, b) 3D model of an array of hematite coated nano-pyramids.

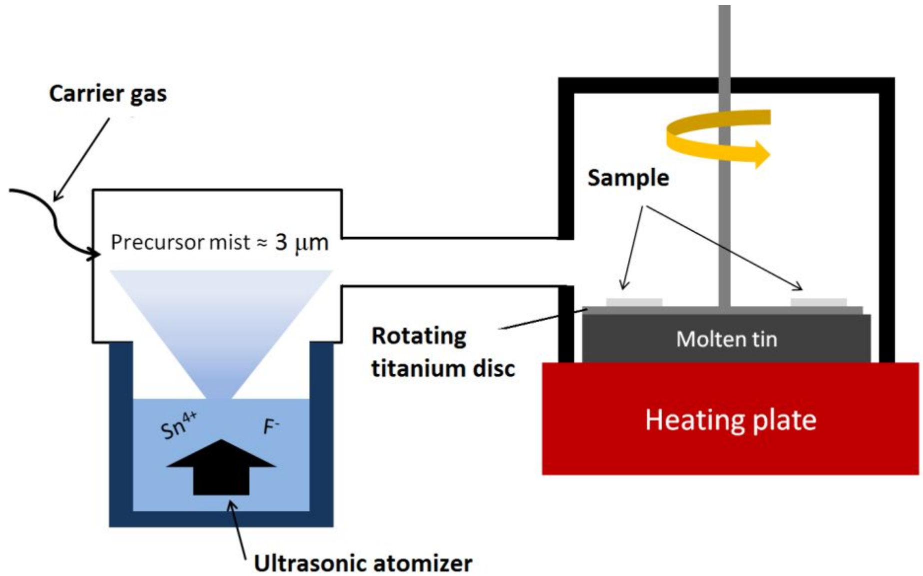

Figure S2. Scheme of the home-built horizontal ultrasonic spray pyrolysis (USP) setup, consisting of an atomization unit (left) directly connected to the reaction chamber (right).

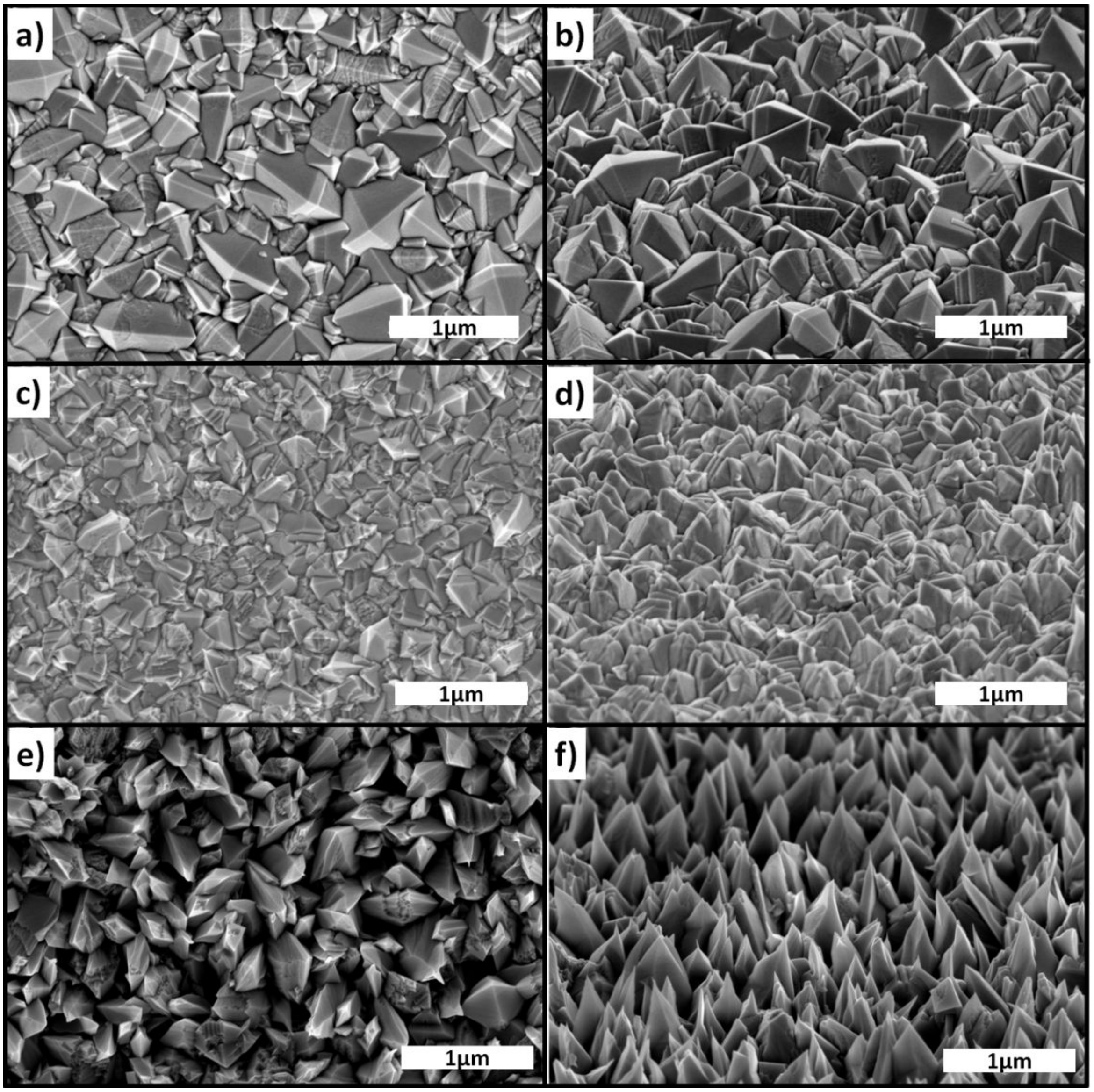

Figure S3. Scanning electron microscopy (SEM) images of a series of 3D FTO samples prepared by ultrasonic spray pyrolysis (USP) at different temperatures during 25 min. a) and b) 450 °C, c) and d) 500 °C, e) and f) 550 °C.

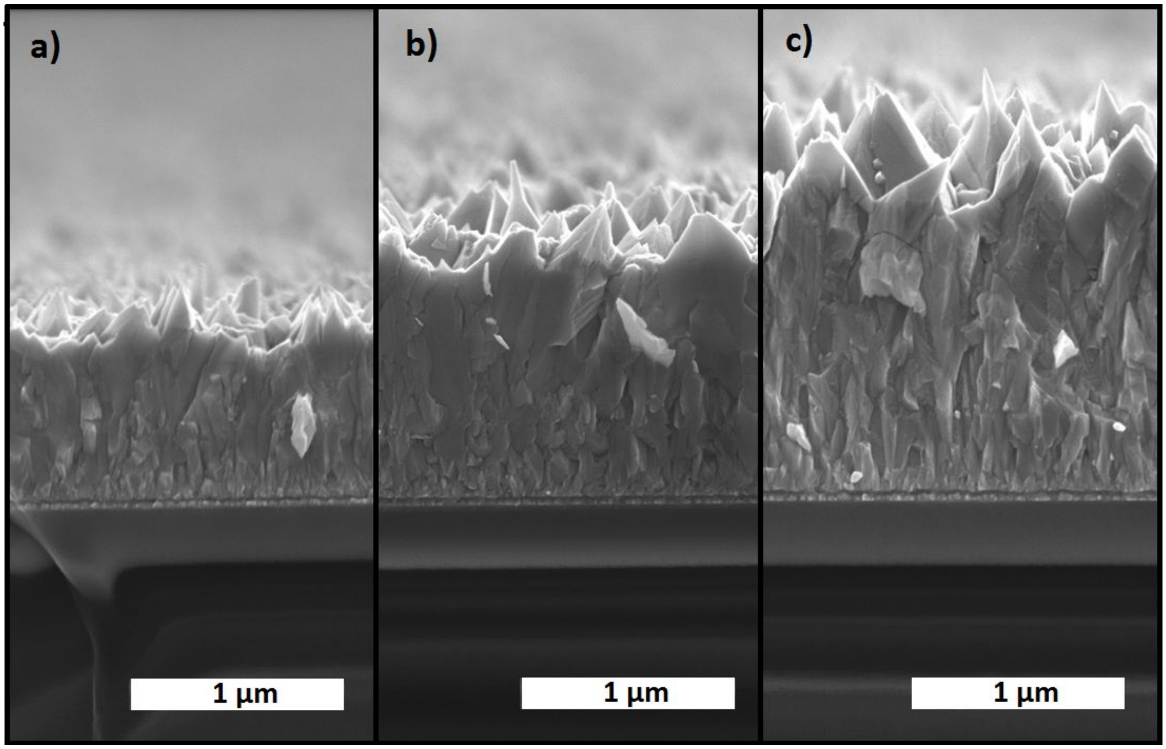

Figure S4. Scanning electron microscopy (SEM) cross section images of a series of 3D-FTO samples prepared at 550 °C and at different deposition times: a) 15 min, b) 20 min, c) 25 min. The scale bar is the same in all three images.

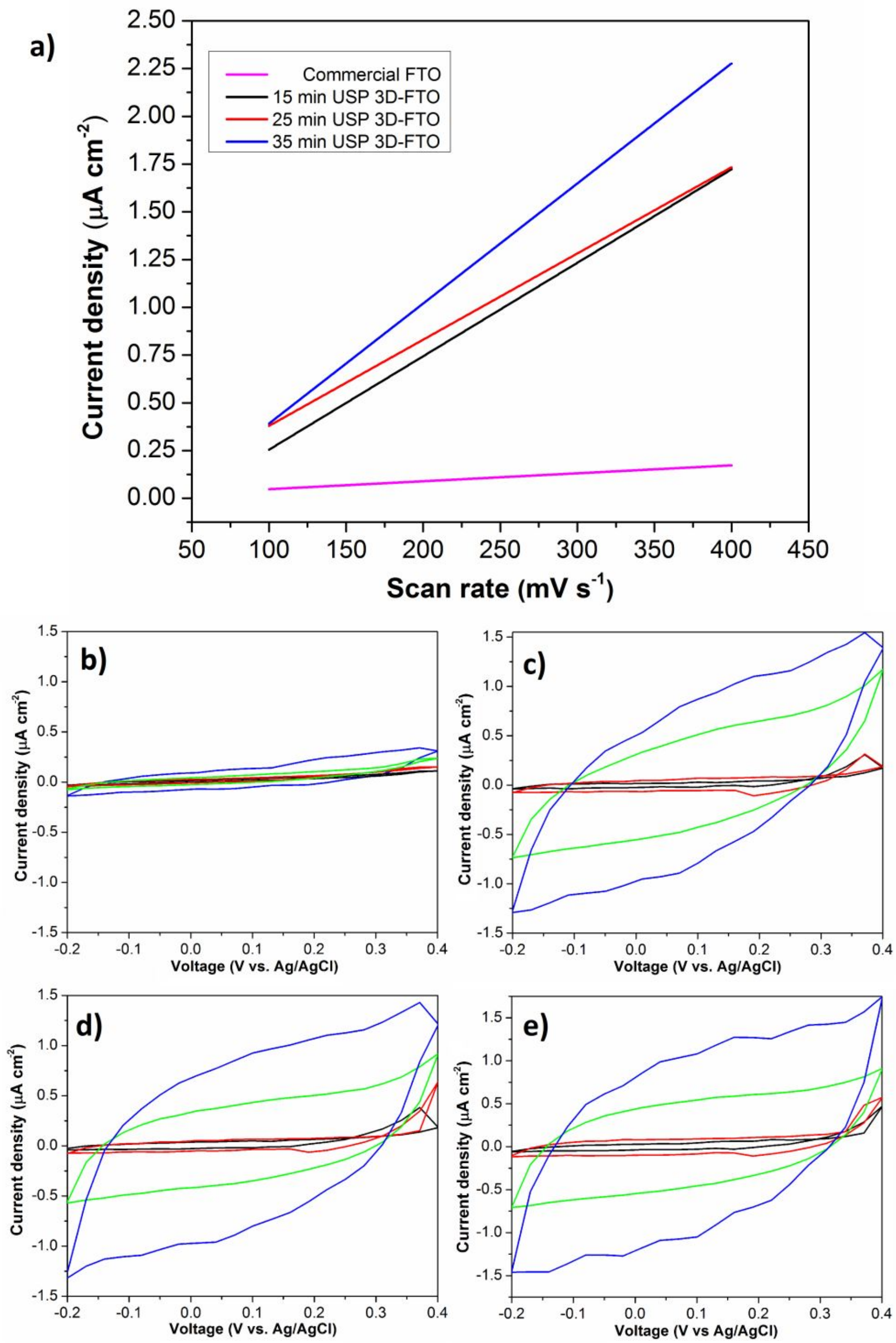

Figure S5. a) Capacitive current densities of bare 3D-FTO and commercial TEC 15 FTO extracted from the cyclic voltammetries at +1.10 V vs. RHE plotted against the scan rate. b) Cyclic voltammetries of commercial FTO at different scan rates from 100 to 400 mV s^{-1}. c), d) and e) show the cyclic voltammetries of 3D-FTO grown during 15, 25 and 35 min, respectively.

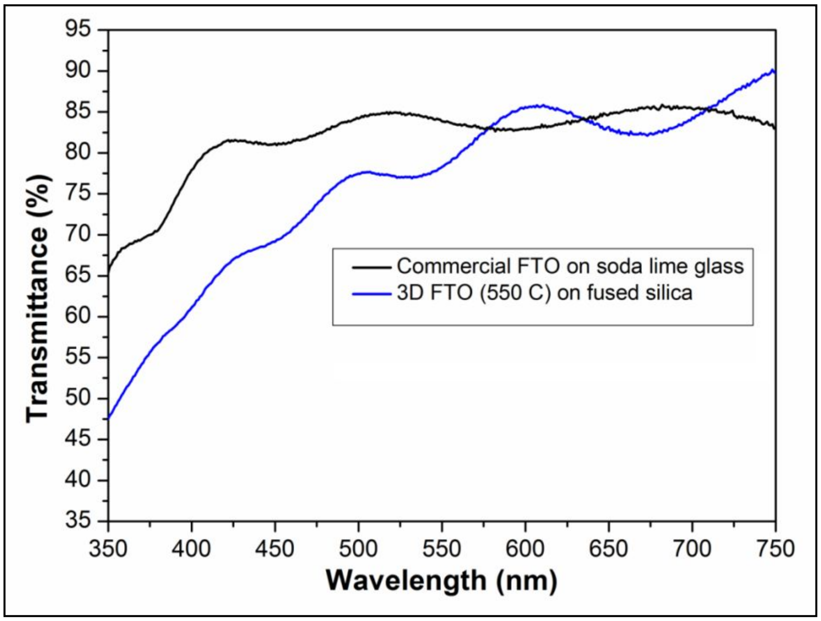

Figure S6. Transmission UV-Vis spectra of a commercial FTO TEC 15 sample (black line) and a 3D-FTO sample prepared at 550 °C and 25 min on fused silica glass (blue line).

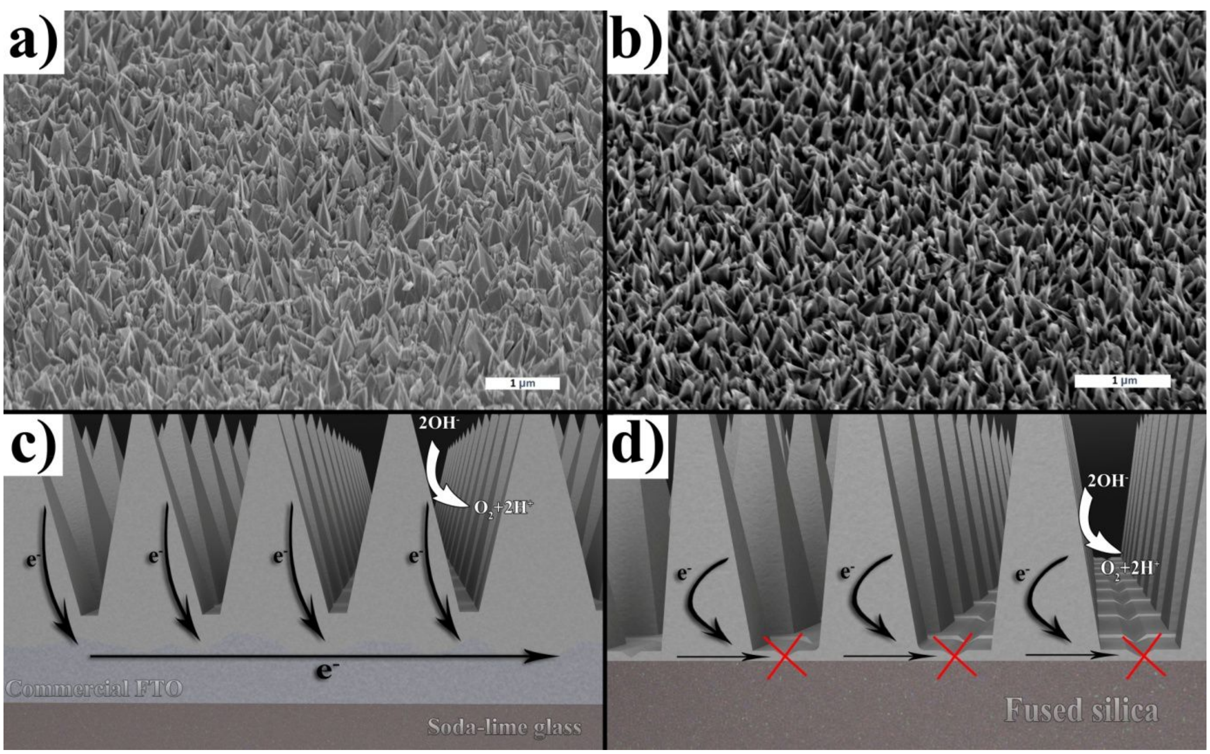

Figure S7. a) Scanning electron microscopy (SEM) image of a 25 min 3D-FTO film grown on commercial TEC 15 FTO. b) SEM image of a 25 min 3D-FTO film grown on fused silica. c) and

d) represent the schematic charge transport mechanism in 3D-FTO grown on commercial TEC 15 and fused silica substrates respectively.

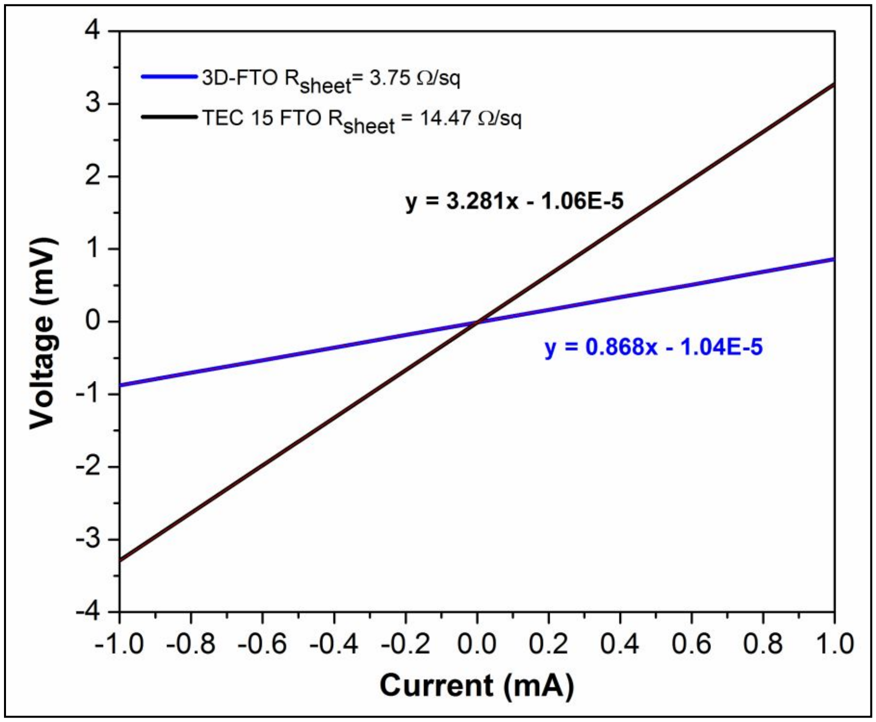

Figure S8. Four-point probe resistivity measurements of commercial FTO TEC 15 and 3D-FTO after 35 min reaction at 550 °C.

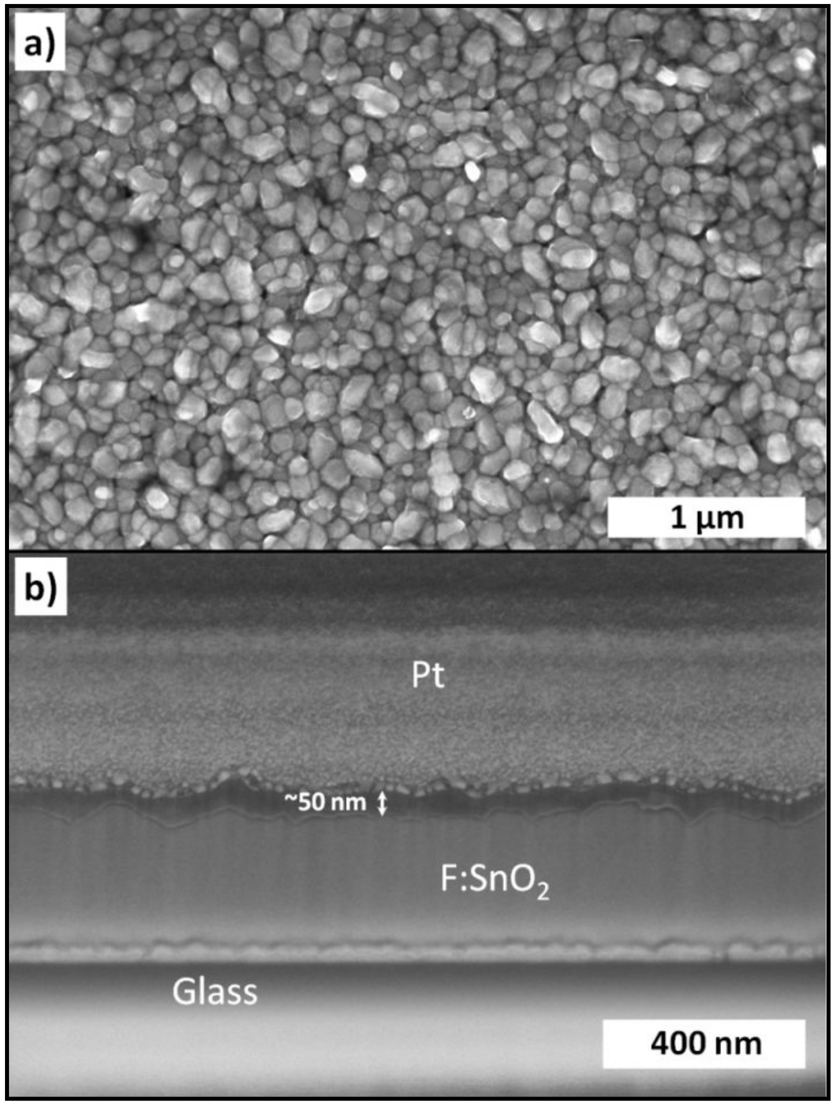

Figure S9. Scanning electron microscopy (SEM) image of a 50 nm thick hematite photoanode prepared by ultrasonic spray pyrolysis (USP) (120 cycles) on commercial FTO TEC 15 and annealed at 550 °C for 2 h and 750 °C for 15 min. a) top view, b) Focused ion beam (FIB)-SEM cross section image.

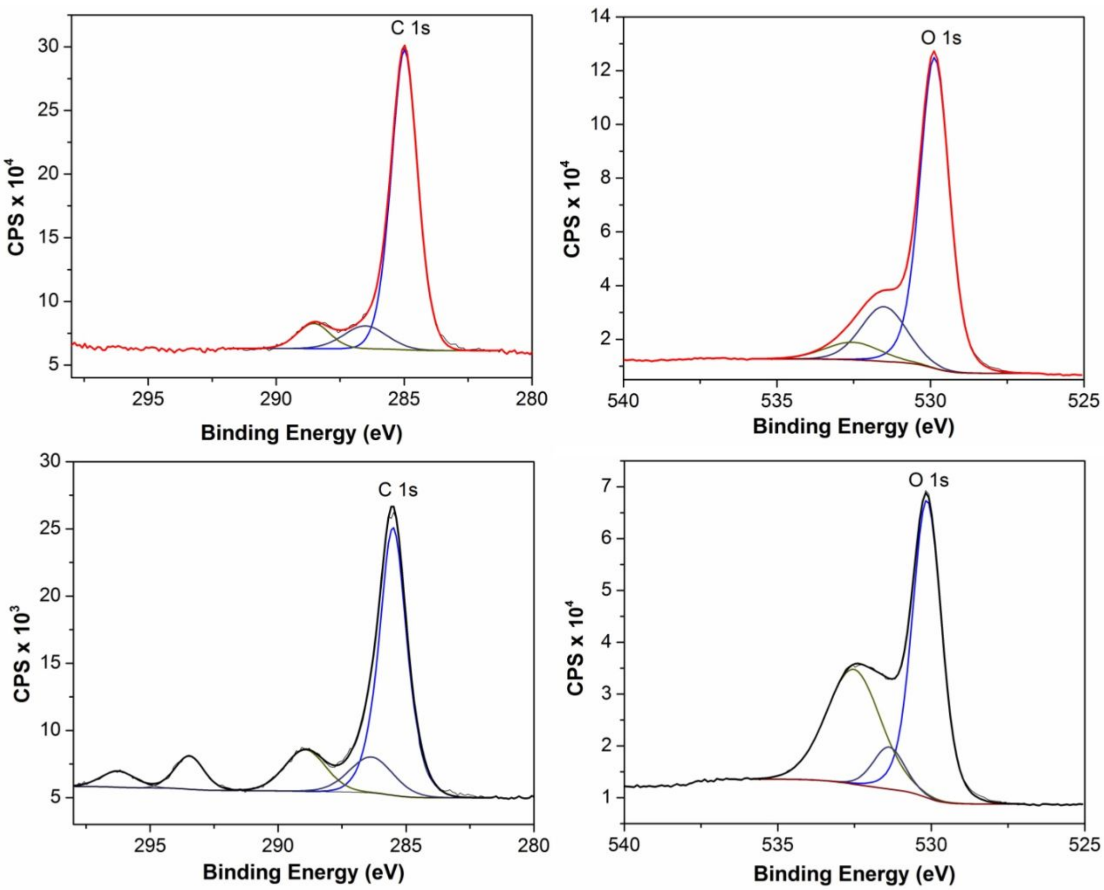

Figure S10. X-ray photoelectron spectroscopy (XPS) data of the C 1s (left) and O 1s (right) edges obtained of hematite samples deposited on commercial FTO (red line) and 3D-FTO (black line) substrates and annealed at 750 °C for 15 min.

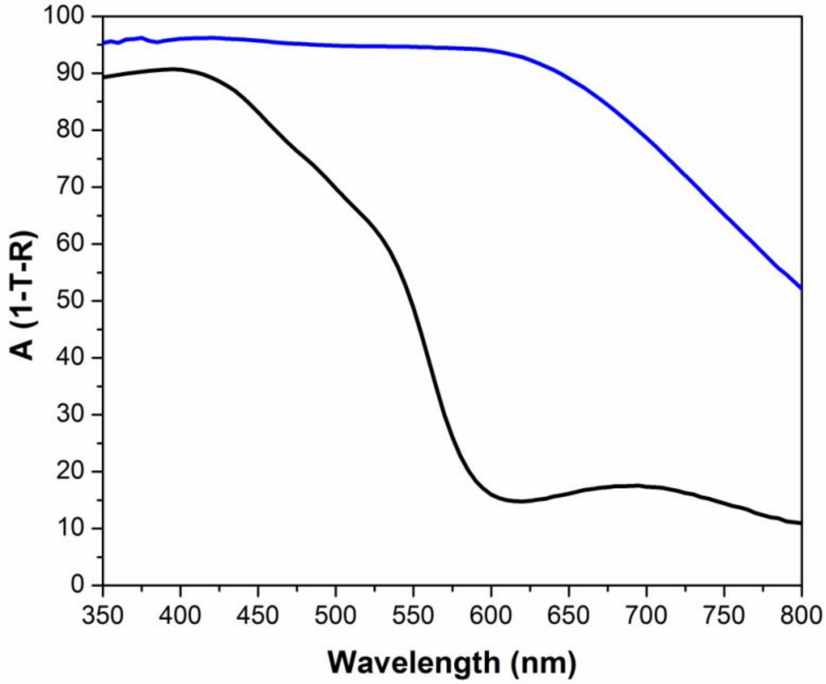

Figure S11. UV-Vis absorption spectra of the hematite thin films on planar and 3D-FTO substrates after annealing at 750 °C.

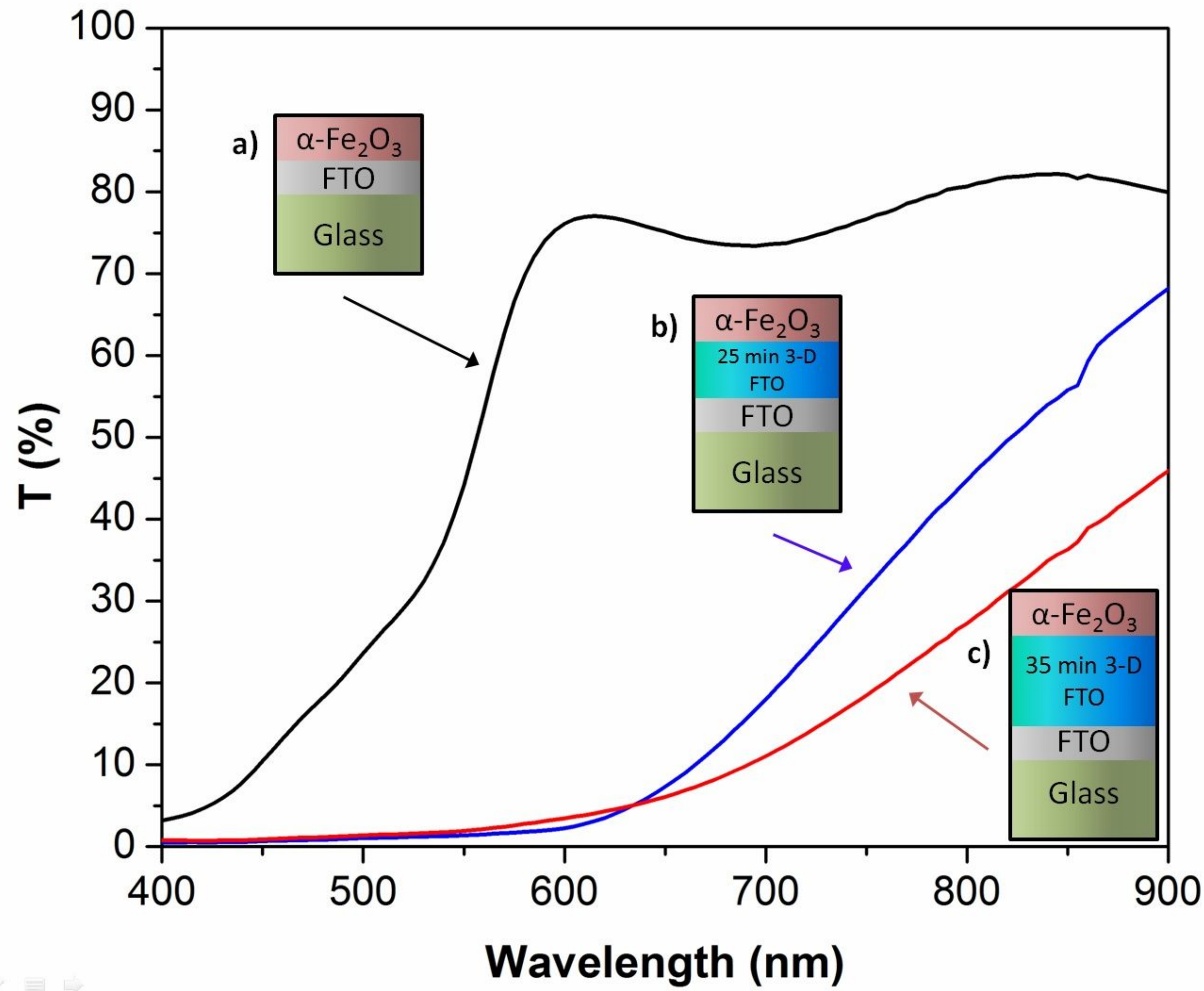

Figure S12. Total transmission UV-Vis-NIR spectra of a hematite thin film deposited onto different FTO substrates. a) commercial FTO TEC 15 sample (black line), b) 3D-FTO sample prepared at 550 °C and 25 min on FTO TEC 15 (blue), c) 3D-FTO sample prepared at 550 °C and 35 min on FTO TEC 15 (red).

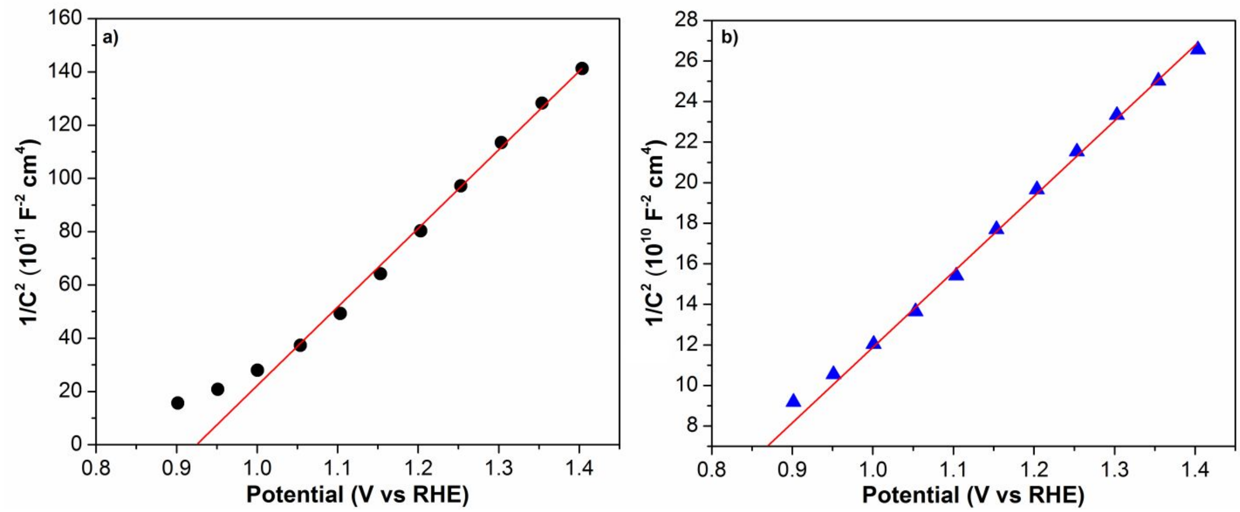

Figure S13. Mott-Schottky plots of inverse square capacitance as a function of potential for a) 50 nm thick hematite photoanode on planar FTO and b) 50 nm thick hematite photoanode on 3D-FTO. Samples were tested in 1 M NaOH at 100 Hz.

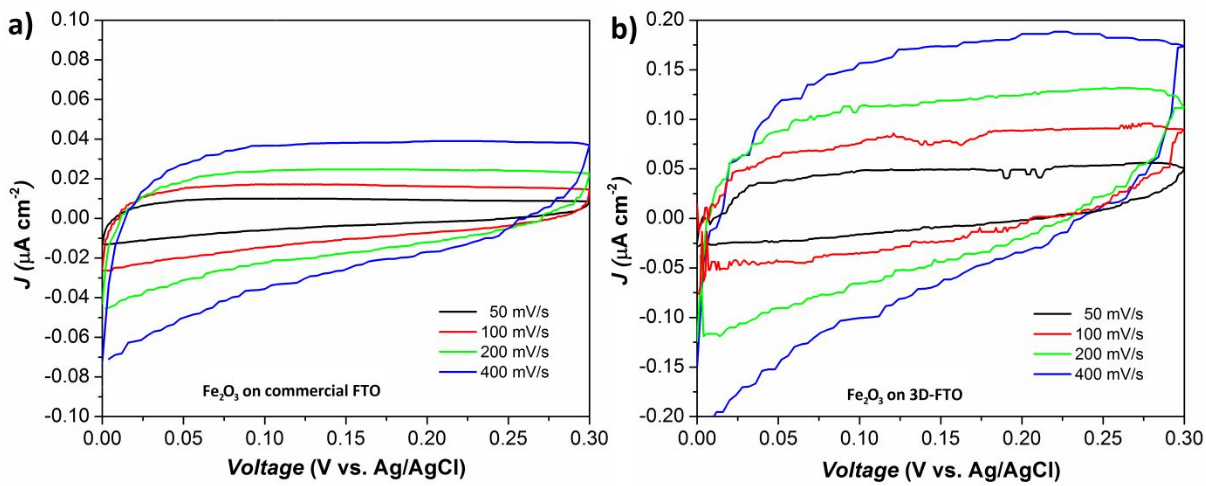

Figure S14. Cyclic voltammetries of a) planar and b) nanostructured hematite photoanodes. Electrolyte was 1 M NaOH.

Table S1. Ratio of Sn:Fe species at the surface and near-surface according to data obtained from angle-resolved X-ray photoelectron spectroscopy (XPS) at take-off angles (ToA) Θ 90° and Θ 10°.

Sample	**Sn/Fe (%)**	
	90 ToA	10 ToA
On 3D-FTO	11	4.6
On Commercial FTO	3.1	4.3